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(71)
PANDEY, Rupesh N.,
34 Old Colony Trail, GUELPH, O1 (CA).
AHMED, Shamsuddin,
247 Cole Road, GUELPH, O1 (CA).
PANDEY, Raj N.,
Chemisar Laboratories Inc.
248 Silvercreek Parkway N., GUELPH, O1 (CA).

(72)
PANDEY, Rupesh N. (CA).
AHMED, Shamsuddin (CA).
PANDEY, Raj N. (CA).

(54) ATTENUATION DES IMPACTS DU DIOXYDE DE CARBONE ET PROCEDE D'UTILISATION DE CE COMPOSE CHIMIQUE PAR FIXATION CHIMIQUE PERMETTANT D'OBTENIR DES PRODUITS DE GRANDE VALEUR

(54) CARBON DIOXIDE MITIGATION AND UTILIZATION PROCESS VIA CHEMICAL FIXATION TO VALUABLE COMMODITIES

(57)
A novel process of capturing and utilization of carbon dioxide from flue gases as a method of reducing the level of carbon dioxide emissions into the atmosphere is disclosed. The carbon dioxide is first chemically captured directly from the emission stream and then transformed into valuable commercial commodities. The capturing process comprises in passing the stream of flue gas through a reactor packed with a bed of capturing agent selected from the group consisting of calcium hydroxide, magnesium hydroxide, iron hydroxide and combinations thereof, at a temperature from about 200.degree. C to about 400.degree. C, a pressure of about 1 atmosphere to about 10 atmosphere and gas hourly space velocity from about 1000 h-1 to about 10,000 h- 1. If desired, CO2 from the flue gas stream can first be separated by a membrane separator and then reacted with capturing agent. The said calcium hydroxide and magnesium hydroxide as capturing agents are synthesized from the group of abundantly available materials consisting of chloride salts of calcium and magnesium of sea water, fluorite/fluorspar (CaF2) mineral and apatite/rock phosphate (impure Ca3(PO4)2) mineral. Iron hydroxide in ferrous form as capturing agent is synthesized from haematite ore of iron present in abundance in earth's crust. The process of transforming the chemically captured carbon dioxide to valuable products is carried out by mixing the said chemically captured CO2 material with a suitable binding agent to form a plastic-like substance which is then compression molded in a pellet press or in an extruder to form mechanically strong, thermally stable and environmentally friendly articles of desired shapes and sizes having numerous potential domestic and engineering applications, enabling a permanent fixation of carbon dioxide. ss on the han

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(72) PANDEY, Raj N., CA
(72) AHMED, Shamsuddin, CA
(72) PANDEY, Rupesh N., CA
(71) PANDEY, Raj N., CA
(71) AHMED, Shamsuddin, CA
(71) PANDEY, Rupesh N., CA

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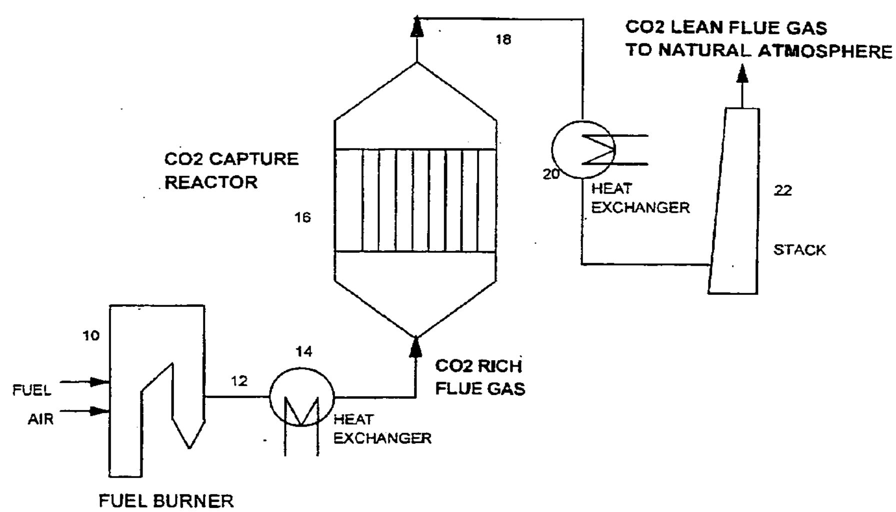
(54) **ATTENUATION DES IMPACTS DU DIOXYDE DE CARBONE ET PROCEDE D'UTILISATION DE CE COMPOSE CHIMIQUE PAR FIXATION CHIMIQUE PERMETTANT D'OBTENIR DES PRODUITS DE GRANDE VALEUR**

(54) **CARBON DIOXIDE MITIGATION AND UTILIZATION PROCESS VIA CHEMICAL FIXATION TO VALUABLE COMMODITIES**



(57) A novel process of capturing and utilization of carbon dioxide from flue gases as a method of reducing the level of carbon dioxide emissions into the atmosphere is disclosed. The carbon dioxide is first chemically captured directly from the emission stream and then transformed into valuable commercial commodities. The capturing process comprises in passing the stream of flue gas through a reactor packed with a bed of capturing agent selected from the group consisting of calcium hydroxide, magnesium hydroxide, iron hydroxide and combinations thereof, at a temperature from about 200° C to about 400° C, a pressure of about 1 atmosphere to about 10 atmosphere and gas

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ABSTRACT

A novel process of capturing and utilization of carbon dioxide from flue gases as a method of reducing the level of carbon dioxide emissions into the atmosphere is disclosed. The carbon dioxide is first chemically captured directly from the emission stream and then transformed into valuable commercial commodities. The capturing process comprises in passing the stream of flue gas through a reactor packed with a bed of capturing agent selected from the group consisting of calcium hydroxide, magnesium hydroxide, iron hydroxide and combinations thereof, at a temperature from about 200° C to about 400° C, a pressure of about 1 atmosphere to about 10 atmosphere and gas hourly space velocity from about 1000 h^{-1} to about 10,000 h^{-1}. If desired, CO_2 from the flue gas stream can first be separated by a membrane separator and then reacted with capturing agent. The said calcium hydroxide and magnesium hydroxide as capturing agents are synthesized from the group of abundantly available materials consisting of chloride salts of calcium and magnesium of sea water, fluorite/fluorspar (CaF_2) mineral and apatite/rock phosphate (impure $Ca_3(PO_4)_2$) mineral. Iron hydroxide in ferrous form as capturing agent is synthesized from haematite ore of iron present in abundance in earth's crust. The process of transforming the chemically captured carbon dioxide to valuable products is carried out by mixing the said chemically captured CO_2 material with a suitable binding agent to form a plastic-like substance which is then compression molded in a pellet press or in an extruder to form mechanically strong, thermally stable and environmentally friendly articles of desired shapes and sizes having numerous potential domestic and engineering applications, enabling a permanent fixation of carbon dioxide .

BACKGROUND OF THE INVENTION

This invention relates generally to the abatement and mitigation of carbon dioxide emissions from power generation, incineration, heating and transportation sectors which use fossil fuels as the energy source and during the process emit CO_2 in natural atmosphere. In particular, it relates to a novel and cost-effective method of capturing carbon dioxide at source from flue gas streams and of utilizing the captured carbon dioxide by transforming it into economically viable and environmentally friendly commodity.

Anthropogenic emissions of carbon dioxide arising mainly due to combustion of fossil fuels, resulting in CO_2 emissions of about 22 billion tons per year, and deforestation (about 7 billion tons per year) is causing a steady increase in global atmospheric concentration of carbon dioxide. It is predicted that this increase of carbon dioxide in the atmosphere will cause the earth's temperature to rise by an amount larger than that occurred over the past 9,000 years. This global warming effect is likely to bring about significant changes in local climate conditions leading to possible loss of arable land, rise in sea level with associated coastal flooding, and increase in ground-water salinity. It may also exacerbate the photochemical smog problem. Thus, there is a need for early action to develop methods for abatement and mitigation of emissions of carbon dioxide, which is the principal Green House Gas (GHG) contributing to global warming. This need has been recognized in the recent global conference on climate change held in Kyoto (December, 1997) in which various countries have agreed to significant reduction of greenhouse gas emissions in the very near future. The U.S. alone is responsible for almost quarter of global carbon dioxide emissions amounting to about 20 tons per year per person. At the present time, it is of paramount importance to develop technology for net CO_2 mitigration in order to combat emissions of Green House Gases (GHG).

Possible Strategies for Mitigation of CO_2 Emissions

Many possible strategies to reduce the build-up of CO_2 levels in the atmosphere are discussed in the literature (P. Freund, Waste Management, 17, 281 (1997). These include: i) improvements in energy efficiency and fuel switching; ii) introduction of renewable sources of energy or nuclear power to displace fossil fuels; iii) CO_2 capture and storage; and iv) CO_2 capture and utilization by making chemicals.

Improvements in Energy Efficiency and Fuel Switching

The increase of energy efficiency of primary energy generating system and/or switching to a fuel with lower carbon to hydrogen ratio (for example, coal to natural gas) can provide useful reductions in CO_2 emissions by producing lesser amounts of CO_2 for the same energy output. Current power generating systems operate at 30-40% efficiency. Increasing energy efficiency, however, requires substantial capital investment. Also there are practical limits to achievable efficiencies at reasonable costs. Restricting the usage to a specific type of fossil fuel is also not a viable option on a long-term basis due to availability considerations. In any case, energy efficiency improvements or fuel switching to low carbon fuels can only offer short-term solutions because CO_2 reductions by these means although would initially be substantial, they will have diminishing impact over long-range.

Introduction of renewable energy or nuclear power

Switching to renewable energy or nuclear power can provide deep reductions. However, it is to be understood that the world is so much dependent on fossil fuels that it is important that there should also be a technology option which would permit continued use of fossil fuels with much less emissions of CO_2.

Capture and Storage of CO_2

The possibility of reduction of CO_2 emission by capture and storage of CO_2 from flue gases is also receiving considerable attention. According to this process, after the combustion of fossil fuels (for power generation, etc.), CO_2 is to be separated and recovered, and then be stored for a long time.

There is a wide range of possible CO_2 separation and recovery techniques: (i) gas/liquid scrubbing (adsorption) ; (ii) gas-solid adsorption ; (iii) cryogenic fractionation ; and (iv) membrane separation. Each of these capturing techniques has its own advantages and disadvantages. However, the most important point to take into account is that the CO_2 capture, regardless of the technique used, is an expensive process. Actual costs are source and fuel dependent. For example, in case of power generation, capturing is projected to increase the cost of electricity generation by at least 40 - 50% above current levels.

Several possible methods of long-term storage of the separated and recovered CO_2 from flue gas

are being discussed. These methods include: i) ocean storage ; ii) underground (depleted oil and gas reservoirs) storage; and iii) growth of forest.

In nature the oceans and seas constitute important CO_2 sink and have large storage capacities. However, there are a number of uncertainties associated with this option such as ecological impact on the ocean environment, final fate of injected CO_2 or how long CO_2 would remain in the deep ocean. In other words, a full understanding of the complex chemical, biological and oceanographic factors has to be acquired before proposing such an option. Also not all countries have suitable access to deep oceans.

It is also possible to store large quantities of CO_2 in underground reservoirs consisting of exhausted oil or gas fields. The possible implications of this type of storage (for example, due to possible reaction between CO_2 and host rock in the underground reservoir) are unknown. Also, it remains to be seen if this storage can provide a long-term fixation of CO_2.

Ocean and underground storage as discussed above, deals with possible means of end-of-pipe removal of CO_2. As an alternative, removal of CO_2 from the atmosphere by enhancing the take-up by natural sinks, typically by growing forests, is also being discussed. However, availability of massive amount of land for such afforestation and reforestation and their possible impact are in question and delays in rate of utilization is inadmissibly long.

Utilization of CO_2 (Chemical Fixation)

The most preferred route to mitigate CO_2 emissions into the atmosphere is to utilize the captured CO_2 to make chemical products in which there is a net reduction of CO_2 during the product formation and utilization. This approach is receiving considerable attention. Various available methods to recycle CO_2 to produce fuels, fuel additives, or fuel precursors such as syngas (CO/H_2 mixture), methanol, MTBE (methyl tert-butyl ether), DMC (dimethyl carbonate), or DME (dimethyl ether) do not necessarily result in CO_2 reduction. Some of these processes are commercially practiced and the technology is mature. In the context of mitigating CO_2 emissions, it should be noted that these processes are highly endothermic requiring large energy input in the product formation. If this energy is supplied by the combustion of a carbon based fossil fuel, then CO_2 would again be generated and emitted to the atmosphere, which has to be taken into consideration in the overall CO_2 mass balance. Edwards (see J.H. Edwards, Catalysis Today, 23,59 (1995)) critically analyzed overall CO_2 mass balance of many CO_2 based fuel producing reactions and concluded that unless the energy (and, in some cases, co-reactant

hydrogen) required for the CO_2 conversion process is derived from non-fossil fuel sources, there is little or no net reduction of CO_2 emissions in recycling CO_2 from existing sources.

It is evident that currently perceived strategies for abatement and mitigation of carbon dioxide as known to the art have numerous uncertainties and difficulties. One prospect that could offer significant advantages is the capture process provided it could be performed economically without additional fossil fuel consumption (i.e. net CO_2 reduction) and provided the captured CO_2 could be utilized for making environmentally friendly value added products so as to provide an economic incentive to industries world-wide to act voluntarily towards reducing GHG (Green House Gas).

It is therefore an object of this invention to provide a novel and alternative cost-effective process for capturing carbon dioxide emissions from stationary or mobile sources.

It is another object of this invention to provide a method of transforming captured CO_2 to valuable product. The captured CO_2 remains permanently fixed in this transformed product, which is thermally stable, mechanically strong, non-flammable and does not release toxic gases.

SUMMARY OF THE INVENTION

According to this invention, the emission streams containing CO_2 are chemically interacted with the capturing agent of this invention forming a material hereinafter referred to as "CHEM-CO_2" (chemically captured CO_2). CHEM-CO_2 is then directly transformed into articles or bodies having different potential applications, without producing CO_2 in the transformation process. These articles or bodies obtained by transforming the chemically captured CO_2 (CHEM-CO_2) into value added products are, for convenience, hereinafter referred to as "CHEM-CO_2-P". The method of this invention is superior to other currently considered methods of reducing CO_2 emissions involving chemical utilization for fuel because these other methods, unlike the method of this invention, generate CO_2 in the product formation and utilization.

The process is given a trade name "CARBO-FIX".

BRIEF DESCRIPTION OF THE DRAWINGS

The objects, features and advantages of the present invention will become apparent from the following description reference being made to the following figures in which:

FIG. 1. is an illustration of a method of insitu capture of CO_2 for utilization in accordance with one embodiment of the invention.

FIG. 2. is an illustration of a variation of the method of capture of CO_2.

FIG. 3. is an illustration of the preferred embodiment on the utilization of the captured CO_2.

DESCRIPTION OF THE INVENTION

This invention relates to a novel process of capturing and utilization of CO_2 from flue gas streams in order to reduce CO_2 emissions in the atmosphere. The process steps include:

a) passing the flue gas through a reactor packed with a bed of CO_2 capturing agent of this invention; and

b) transforming chemically captured CO_2 (CHEM-CO_2) formed in the capturing step (a) above into value added articles (CHEM-CO_2-P) by mixing it with a suitable binding material and molding the mix in a pelleting press or in an extruder.

Preferred embodiment on capture of CO_2

A first embodiment of the invention relates to a novel method of capturing CO_2 from flue gas stream by allowing the flue gas to pass through a reactor containing a bed of capturing agent. The said capturing agent according to this invention is selected from the group consisting of calcium hydroxide, magnesium hydroxide, iron hydroxide and combinations thereof. The capturing reaction is carried out at a temperature ranging from about 150 to about 450° C. The reaction is conveniently carried out at atmospheric pressure, although elevated pressure may also be used. The flue gas stream is passed through the bed of capturing agent at a gas hourly space velocity (GHSV) ranging from about 1,000 to 10,000 h^{-1}. The capturing agent is charged in the reactor in the granular form, although pellet or honeycomb monolith forms may also be used.

Applicants have found that the treatment of flue gas with the capturing agents specified above and according to the procedure described above can lead to substantial reductions in carbon dioxide emissions from the flue gas. The capturing process of this invention can be applied to the abatement and mitigation of the emission of carbon dioxide from different types of power generation power plants including those of pulverised fuel and flue gas desulphurisation (PF-FGD), natural gas fired combined cycle /gas turbine combined cycle (GTCC) and integrated gasification combined cycle (IGCC). It is also applicable to industrial boilers, municipal waste

incinerators, cogenerators, heating and transportation sectors, and miscellaneous industrial sources of CO_2 emissions including mining, metallurgical, cement and fertilizer production processes.

The following reactions represents the CO_2 capturing/removal pathways from the flue gas when $Ca(OH)_2$ is used as the capturing agent:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
$$Ca(OH)_2 \longrightarrow CaO + H_2O$$
$$CaO + CO_2 \longrightarrow CaCO_3$$

According to one preferred aspect of the first embodiment, enormous supply of calcium hydroxide and magnesium hydroxide essential to accomplish large-scale capture of CO_2 from flue gases can be obtained from the following naturally occurring sources: i) chloride salts of calcium and magnesium present in abundance in sea water; ii) fluorite/fluorspar (CaF_2) mineral; and iii) apatite/rock phosphate (impure $Ca_3(PO_4)_2$ mineral. Because these sources are not carbonate salts or minerals, synthesis of hydroxides of calcium or magnesium do not cause emissions of CO_2. The soluble chloride salts of calcium and magnesium are converted to corresponding insoluble hydroxides by hydrolysis reactions under alkaline conditions according to known wet chemical methods, which are then easily recovered from the aqueous medium by filtration. Fluorite and apatite minerals can also be converted to calcium hydroxide by conventional wet chemical methods.

According to another preferred aspect of the first embodiment, dissolved chloride salts of calcium and magnesium from the sea water are recovered by evaporation using solar energy. The use of natural solar energy avoids the use of fossil fuel based energy sources and therefore not only avoids generation of carbon dioxide but also offers substantial cost savings.

According to another preferred aspect of the first embodiment, enormous supply of iron hydroxide (one of the capturing agent of this invention) essential to accomplish large-scale capture of CO_2 from the flue gas according to the method of this invention can be obtained from haematite (Fe_2O_3) which is the most common ore of iron, the fourth most abundant element (by weight) making up the crust of the earth. Haematite ore can be converted to iron hydroxide by conventional wet chemical methods.

In the insitu capture process which is schematically illustrated in Fig. 1, the CO_2 rich flue gas produced in the fuel burner 10 by combustion of coal or natural gas fuel and discharged via line

12 is passed through a heat exchanger 14 for recovering most of the heat generated by the fuel combustion and also for lowering the temperature of flue gas stream to about 150 - 450° C, and then sent to the CO_2 capture reactor 16 containing a fixed bed of capturing agent chosen from the group consisting of $Ca(OH)_2$, $Mg(OH)_2$ and $Fe(OH)_2$ or a combination thereof. As CO_2- rich flue gas passes through the capturing agent bed maintained at a temperature of 150 - 450° C, CO_2 of the flue gas reacts with the capturing agent forming CHEM-CO_2 and remains permanently fixed to it. Thus the flue-gas exiting the capturing reactor contains substantially lesser amount of CO_2 than the flue gas entering the reactor. The effluent stream from the capturing reactor discharged via line 18 is passed through a heat exchanger 20 for recovering useful heat and then through a stack 22 before being vented at a regulatory height to the natural atmosphere. When the bed of capturing agent becomes fully saturated with CO_2, it is removed from the reactor and a fresh batch of capturing agent is loaded into the reactor.

According to a preferred variation of the first embodiment, if desired, CO_2 from the flue gas stream can first be separated by a membrane process, and then captured with the capturing agents of this invention. For use in the process of this invention, the package of membranes (fabricated from suitable glassy and rubbery polymers) is preferrably placed in the membrane separator in a plate-and-frame configuration, as illustrated by way of example in Figure 2. For gas separations, traditionally, membranes are used in tubular, spiral-wound and hollow-fiber forms. All of these forms, however, have drawbacks. The tubular form has a very low membrane surface area per unit packing volume and consequently would produce a flux (flux is the rate of permeation through the membrane expressed, for example, in cubic metres of gas per hour) which is far too low to be of practical significance. The hollow-fiber and spiral-wound forms of membrane offer the desired high membrane surface areas, but create large pressure drops in the bulk flow directions, thus requiring high inlet pressure and low flow velocity for their operation. Consequently, membranes of hollow-fiber and spiral-wound configurations are not suitable for low pressure and high velocity flue gases produced by power plants, industrial boilers, etc. On the other hand, the conceptual plate-and-frame membrane module of this invention would offer several advantages: it is simple and compact; pressure drop would be relatively low; there would be no need for flue gas pressurization; it would allow treatment of flue gases of high flow velocities; it would maintain structural integrity against high pressure; and it would allow easy replacement of fouled membrane elements.

As illustrated in Fig. 2, the conceptual membrane separator consists of housing 1 having inlet 2 for introducing feed gas mixture (flue gas). The membrane package consisting of several flat symmetric or composite gas-separation membranes 3 (a symmetric or composite membrane

consists of a thin separating layer supported on thick porous substrate) having holes 4 in the centre are placed in the housing 1. The central holes 4 coincide with the collector channel 5 which, in turn, is connected with outlet 6. Carbon dioxide of flue gas preferentially permeating through gas-separation membranes 3 is collected in collector channel 5 and exits via outlet 6. Between each pair of membranes 3 are gas-impervious diaphragms 7 with the central holes 8 that coincide with collector channel 5. Alternating membranes and diaphragms are packed with strips 9 in the housing 1. The retentate exits via second outlet 10.

The separated CO_2 exiting the membrane separator of preferred plate-and-frame configuration is sent to the capture reactor where it reacts with the capturing agent of this invention forming CHEM-CO_2, which is then utilized to produce valuable chemical commodities (CHEM-CO_2-P) as described below under second main embodiment of this invention.

Preferred embodiment on utilization of captured CO_2

A second main embodiment of the invention relates to a method of utilization of the captured CO_2. It involves the transformation of the CHEM-CO_2 (chemically captured CO_2), as defined earlier, into CHEM-CO_2-P, which as defined earlier, are mechanically strong articles of different shapes and sizes, having numerous potential applications. The method, as illustrated in accompanying Fig. 3, consists of following steps:

(a) grinding CHEM-CO_2 into a fine powder;

(b) mixing the powder of step (a), without loss of CO_2, with an aqueous dispersion or aqueous solution of a suitable inorganic or organic binding material;

(c) partially drying the powder-binder mix to yield a plastic-like material of desired consistency;

(d) fabricating mechanically strong shaped bodies either by compression molding of the material of step (c) in a pelleting press or by extrusion molding with a suitable extruder; and

(e) totally drying the pellets or extrudates at a temperature of about 80° C to about 140° C in air atmosphere.

Applicants have found quite unexpectedly that binding and consolidation of CHEM-CO_2 materials, according to the procedure described above, produce articles of different shapes and sizes (CHEM-CO_2-P), which exhibit a number of desirable properties: good mechanical strength,

non-flammability and fire resistibility, good thermal stability, no tendency to re-release CO_2 upon storage, and no emissions of toxic gases or vapours upon storage. These attributes make CHEM-CO_2-P suitable for application in diverse areas such as household decorations, appliances, business and office machines, scientific instruments, electronic equipments, etc.

In one preferred aspect of the second main embodiment of the invention, the binding material used in step (b) above is selected from the group consisting of inorganic binders such as bentonite clay, attapulgite clay, kaolin clay, sepiolite clay, silica sol and combinations thereof, or from the group consisting of thermoplastic or thermosetting organic polymers/resins such as polyvinyl alcohol, polypropylene, polyethylene and combinations thereof, or from the group consisting of gellable organic binders such as methylcellulose, ethylcellulose, hydroxymethylcellulse, hydroxyethylcellulose, hydroxybutylcellulose, carboxymethylcellulose and mixtures thereof. The binding material used in step (b) can also be an admixture of an inorganic binder chosen from the substances specified above and an organic binder chosen from the substances specified above.

The preferred binders to use in the practice of the present invention are clay materials such as bentonite, kaolin, attapulgite and sepiolite. They are chosen because they offer a number of advantages: i) they exhibit excellent binding and agglomerating property; ii) they are naturally occuring substances available in abundance worldwide; iii) they exhibit high thermal stability being stable even at a temperature of 500° C; and iv) they do not release toxic gases or vapours upon storage or exposure to elevated temperature.

In another aspect of the second main embodiment, in making value-added articles with CHEM-CO_2 (e.g. $CaCO_3$ resulting from capturing CO_2 with $Ca(OH)_2$), the binder is used in the amount ranging from about 5% to about 30% based on the weight of CHEM-CO_2. The higher the binder content, the greater is the mechanical strength of the formed shaped article (CHEM-CO_2-P).

The following non-limiting examples are provided to further illustrate the invention.

EXAMPLE 1
Capturing of Carbon Dioxide

A sample of $Ca(OH)_2$, in the form of a fine powder, was moistened with water and a paste made of. The paste was dried in an oven at a temperature of about 100° C to form hardened lumps, which were then broken to form granules of $Ca(OH)_2$.

A glass microreactor was packed with 1.0 gram of the granular $Ca(OH)_2$ prepared as above and placed in a continuous flow system. A feed gas mixture consisting of, by volume, 30% CO_2, 5% O_2 and 65% N_2 was continuously passed at a flow rate of 27.5 mL/min (STP) through the $Ca(OH)_2$ bed maintained at the desired reaction temperature. The reactor was maintained at 1 atmosphere. As the feed mixture passes over the bed, $Ca(OH)_2$ captures CO_2 from the mixture by chemically reacting with it and is converted to CHEM-CO_2, which in the present instance is $CaCO_3$. The reaction was carried out at 200, 300, 400 and 450° C, starting with a new sample of the capturing agent, $Ca(OH)_2$, at each temperature. At each temperature, the capturing reaction was allowed to proceed for a definite period of time.

At the end of each experiment, the reactor was cooled to room temperature, the resultant CHEM-CO_2 removed and analyzed for its carbon content using a CHN elemental micro-analysis apparatus. From the carbon content of the product and the total volume of CO_2 passed through the solid bed over the reaction period, and assuming that the capture reaction stoichiometry is $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$, the percentage of CO_2 captured (or removed) from the feed gas mixture and the percentage of $Ca(OH)_2$ converted to $CaCO_3$ due to the capturing reaction were calculated. The results are summarized in Table 1.

TABLE 1

CO_2 capturing by $Ca(OH)_2$

Reaction temperature (°C)	Contact Time	Carbon in the Product (%)	$Ca(OH)_2$ converted (%)	CO_2 removed from feed mixture (%)
200	2 sec	3.573	29.8	1.7
300	2 sec	4.808	40.0	2.6
400	2 sec	8.232	69.0	19.3
450	2 sec	9.940	82.8	24.2

It is apparent from Table 1 that at temperatures of 400° C and above, significant removal of CO_2 from feed gas mixture is achieved. By <u>increasing the contact time, the CO_2 removal can be further increased</u> and maximized. It may be noted that in real situations the total removal of CO_2 is not necessary in combating GHG emissions, nor is it desirable from ecological considerations.

EXAMPLE 2
Capturing of Carbon Dioxide

The capturing agent for the cases included in this example was granular $Ca(OH)_2$ prepared as described in Example 1.

The reaction was carried out in a stainless steel batch reactor, having an internal volume of 75 mL. The reactor had provisions for filling it with the feed gas mixture and for withdrawal of the gas sample for analysis by gas chromatography. A weighed amount of sample (0.75 - 1.5 g) of granular $Ca(OH)_2$ was loaded in the reactor. The reactor was purged and then filled with a feed gas mixture, consisting of 30% CO_2, 5% O_2, and 65% N_2, to a pressure of 25 psi. A sample of the feed gas mixture (0.2 mL) was withdrawn from the reactor with a gas-tight syringe and analyzed by gas chromatography. The reactor was rapidly heated to the desired reaction temperature and the capturing of CO_2 from the feed gas mixture by the capturing agent, $Ca(OH)_2$, was allowed to proceed. Samples of reaction gas mixture (0.2 mL of sample each time) were withdrawn at different reaction times and analyzed by gas chromatography. The percentage of CO_2 removed from the feed mixture due to the capturing reaction, as a function of reaction time, was calculated from gas chromatographic responses of the feed gas mixture and reaction gas mixture using N_2 present in the feed as internal standard. The reaction was carried out at 200 and 250° C, starting with a new charge of $Ca(OH)_2$ at each temperature. The results are summarized in Table 2.

TABLE 2

Capturing of Carbon dioxide
(CHEM-CO_2 Formation)

Reaction temperature (°C)	Reaction time, t (min)	Percent CO_2 Removal from feed
250	10	21.3
	60	99.5
	90	99.7
200	20	49.7
	40	73.5
	75	97.5

note 0.75 g of $Ca(OH)_2$ was used at 250° C tests and 1.5 g of $Ca(OH)_2$ was used at 200° C tests.

It is apparent from Table 2 that the treatment of CO_2 - containing gas mixture with $Ca(OH)_2$ as capturing agent in a batch reactor can over longer reaction times accomplish nearly 100% CO_2

removal at temperatures of 200° C and above.

EXAMPLE 3

Transformation of CHEM-CO_2 into Value-added Commodity

(a) 2.5 grams of polyvinyl alcohol (PVA) binder was dissolved in about 50 mL water. 50 grams of ground $CaCO_3$ (CHEM-CO_2 obtained by capturing of CO_2 with $Ca(OH)_2$ as capturing agent) was added to the PVA solution and thoroughly mixed to form a slurry. The slurry was then partially dried by heating at about 70 - 85° C with occasional stirring to form a plastic-like mass of desired consistency (corresponding to a moisture content of about 10-20% based on the weight of $CaCO_3$). The material was thereafter formed into several pieces of cylindrical shaped pellet of 20 mm diameter and 15-25 mm length by compression molding in a cylindrical die by means of a hydraulic press. Pellets were then dried at about 150° C until constant weight. The final product (CHEM-CO_2-P) was mechanically strong blocks of white appearance. For convenience, this type of CHEM-CO_2-P product is referred to as "$CaCO_3$-PVA bodies" in Example 5 and Example 7 below.

(b) An aqueous suspension of 10 grams of bentonite clay in about 100 mL water was prepared by adding the clay to the water in steps while continuously stirring. 40 grams of $CaCO_3$ (CHEM-CO_2 obtained by the capturing of CO_2 with $Ca(OH)_2$ as capturing agent) was added to the clay dispersion and blended to form a slurry. The slurry was then partially dried by heating at about 70-85° C with occasional stirring to form a plastic-like mass of desired consistency (corresponding to a moisture content of about 10-20% based on the weight of $CaCO_3$). The material was thereafter formed into several pieces of cylindrical shaped pellet of 20 mm diameter and 10-20 mm length by compression molding in a cylindrical die by means of a hydraluic press. Pellets were then dried at about 150° C until constant weight. The final product (CHEM-CO_2-P) was mechanically strong blocks of white appearance. For convenience, this type of CHEM-CO_2-P product is referred to as "$CaCO_3$ - bentonite bodies" in Example 4 and Example 6 below. The appearance could be changed by adding varying colouring agents as desired for decorative articles of commercial value (see example (c) below).

(c) 5 grams of polyvinyl alcohol binder was dissolved in about 50 mL water. To this solution were added 40 grams of $CaCO_3$ (CHEM-CO_2 obtained by the capturing of CO_2 with $Ca(OH)_2$ as capturing agent) and 5 grams of Fe_2O_3, and thoroughly mixed to form a slurry. The slurry was then partially dried by heating at about 70-80° C with occasional stirring to form a plastic-like mass of desired consistency (corresponding to a moisture content of about 10 - 20% based on

the weight of $CaCO_3$). The material was thereafter formed into several pieces of cylindrical shaped pellet of 20 mm diameter and 10-20 mm length by compressing molding in a cylindrical die by means of a hydraulic press. Pellets were then dried at about 150° C until constant weight. The final product (CHEM-CO_2-P) was red coloured mechanically strong blocks.

EXAMPLE 4

Aging Test of CHEM-CO_2-P (obtained with bentonite binder)

To test whether the $CaCO_3$ - bentonite bodies would retain the captured CO_2 over extended periods (as is desirable for any meaningful mitigation and utilization process), these bodies were subjected to accelerated aging by heat treatment at various temperatures.

The dried pellet sample of known weight was heat treated in a muffle furnace at the desired aging temperature in air for 3 hours. It was then cooled to room temperature, weighed and analyzed for carbon content (using CHN elemental microanalyzer). The aging or thermal stability tests were performed at 300, 400 and 500° C, using a separate pellet sample for each temperature. The results are reported in Table 3.

Table 3

Aging Tests for CHEM-CO_2-P (obtained with bentonite binder)

Aging Temperature (°C)	Carbon content (%)	Pellet weight		% Weight loss, $[\frac{Wo-W}{Wo}] * 100$
		Initial, Wo (g)	After aging, W (g)	
Drying at 150°C	9.800	-	-	-
300	9.705	10.715	10.626	0.83
400	9.611	9.776	9.695	0.82
500	9.780	9.046	8.967	0.87

As can be seen in Table 3, carbon content and weight of the $CaCO_3$ - bentonite bodies are virtually unaffected by aging at different temperatures, which indicate that these bodies would not re-release the captured CO_2.

EXAMPLE 5

Aging Test of CHEM-CO_2-P (obtained with PVA binder)

To test whether the $CaCO_3$ -PVA bodies would retain the captured CO_2 over extended periods (as is desirable for a meaningful CO_2 mitigation and utilization process), these bodies were subjected to accelerated aging by heat treatment at various temperatures.

The dried pellet sample of known weight was heat treated in a muffle furnace at the desired aging temperature for 3 hours. It was then cooled, weighed and analyzed for carbon content (using a CHN elemental microanalyzer). The aging or thermal stability tests were performed at 300, 400 and 500° C, using a separate pellet sample for each temperature. The results are reported in Table 4.

Table 4

Aging Tests for CHEM-CO_2-P (obtained with PVA binder)

Aging Temperature (°C)	Carbon content (%)	Pellet weight		% Weight loss, $[\frac{Wo-W}{Wo}] * 100$
		Initial, Wo (g)	After aging,W (g)	
Drying at 150°C	13.744	-	-	-
300	12.345	6.666	6.419	3.7
400	11.812	7.240	6.848	5.4
500	11.863	6.314	5.945	5.8

As can be seen in Table 4, carbon contents of 400° C and 500° C aged samples are the same within experimental errors, indicating that, once captured, CO_2 would be permanently held by these bodies. Losses of carbon content and sample weight observed upon 300° C and 400° C aging are most likely due to partial loss of PVA binder at these temperatures.

EXAMPLE 6

Mechanical Strength Test of CHEM-CO_2-P (obtained with bentonite binder)

In order to find wide range of applications, it is desirable for $CaCO_3$ - bentonite bodies to have sufficient mechanical strength. This test consists of measuring the axial crushing strength of cylindrical shaped bodies in the dried state as well as after having been subjected to hot aging

at different temperatures. Strengths were measured in a screw-thread press connected to an electronic balance. The body was subjected to increasing pressure until it began to disintegrate. The results are summarized in Table 5.

TABLE 5

Mechanical Strength Test of CHEM-CO_2-P (obtained with bentonite binder).

Aging Temperature (°C)	Crushing Strength (kg/cm^2)
As - dried (150°C)	7.3
300	6.5
400	6.4
500	6.4

As can be seen from Table 5, hot aging of bodies does not significantly effect their mechanical strength. It may be noted that the crushing strength of $CaCO_3$ bodies formed without any binder was found to be about 3 kg/cm^2. Thus, it is evident that the addition of bentonite binder significantly reinforced the bodies so formed.

EXAMPLE 7

Mechanical Strength Test of CHEM-CO_2-P (obtained with PVA binder)

In order to find wide range of application, it is desirable for $CaCO_3$-PVA bodies to have sufficient mechanical strength. This test consists of measuring the axial crushing strength of cylindrical shaped bodies in the dried state as well as after being subjected to hot aging at different temperatures. Strengths were measured in a screw-thread press connected to an electronic balance. The body was subjected to increasing pressure until it began to disintegrate. The results are summarized in Table 6.

TABLE 6

Mechanical Strength Test of CHEM-CO_2-P (obtained with PVA binder)

Aging Temperature (°C)	Crushing Strength (kg/cm^2)
As - dried (150°C)	10.2
300	5.0
400	4.8
500	4.8

As can be seen from Table 6, hot aging of bodies significantly lowered their mechanical strength. This is due to partial loss of PVA binder from the bodies upon exposure to high temperatures. It may be noted that the crushing strength of $CaCO_3$ bodies formed without any binder was found to be about 3 kg/cm^2. On the other hand, the crushing strength of dried $CaCO_3$-PVA bodies is greater than 10 kg/cm^2, indicating that binding with PVA causes a significant improvement of mechanical strength of the bodies so formed.

While the invention has been described and illustrated herein by references to various specific materials, procedures and examples, it is understood that the invention is not restricted to the particular materials and procedures selected for that purpose. Numerous variations of such details can be employed, as will be appreciated by those skilled in the art.

CLAIMS

We claim:

1. A novel process of capturing and utilization of CO_2 from flue gas streams as a measure to reduce CO_2 emissions in the atmosphere, which comprises of the following steps:

   (a) passing the flue gas through a reactor packed with a bed of CO_2 capturing agent of this invention; and

   (b) transforming the chemically captured CO_2 material "CHEM-CO_2" formed in step (a) into value-added shaped articles "CHEM-CO_2-P" by mixing it with a suitable binding material and molding the mix in a pelleting press or in an extruder.

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    (a) passing the flue gas through a reactor packed with a bed of CO_2 capturing agent of this invention; and

    (b) transforming the chemically captured CO_2 material "CHEM-CO_2" formed in step (a) into value-added shaped articles "CHEM-CO_2-P" by mixing it with a suitable binding material and molding the mix in a pelleting press or in an extruder.

2. A process as claimed in claim 1 wherein said capturing agent is selected from the group consisting of calcium hydroxide, magnesium hydroxide, iron hydroxide and combinations thereof.

3. A process as claimed in claim 1 wherein said capturing reaction is carried out at a temperature ranging from about 100° C to about 500° C, at a pressure ranging from about 1 atmosphere to about 10 atmosphere and at a space velocity ranging from 1000 h^{-1} to about 10,000 h^{-1} .

4. A process as claimed in claim 2 wherein the said capturing agent is calcium hydroxide.

5. A process as claimed in claim 1, 2 and 4 wherein said calcium hydroxide as a capturing agent is synthesized in enormous quantities (essential for large-scale mitigation of CO_2 emissions) from the group of abundantly available naturally occurring materials consisting of $CaCl_2$ salt present in sea water, fluorite/fluorspar (CaF_2) mineral present in earth's crust and apatite/rock phosphate mineral present in earth's crust by means of conventional wet chemical methods.

6. A process as claimed in claim 1 and 2 wherein said magnesium hydroxide as a capturing agent is synthesized in enormous amounts from abundantly available naturally occurring $MgCl_2$ salt in sea water or from its ore.

7. A process as claimed in claim 1 and 2 wherein said iron hydroxide as a capturing agent is synthesized, in large supply by conventional wet chemical methods, from haematite (Fe_2O_3) which is the most common ore of iron and available in abundance in the earth crust.

8. A process as claimed in claim 5 and 6 wherein said chloride salts of calcium and magnesium are recovered from sea water by evaporation using solar energy thus avoiding the use of fossil fuels which causes emissions of carbon dioxide.

9. A process as claimed in claim 1 which is applicable to capturing and utilization of CO_2 in flue gas streams from utility and industrial boilers, co-generators, municipal waste incinerator, heating and transportation sectors.

10. A process as claimed in claim 1 wherein the said step of transformation of "CHEM-CO_2"

to "CHEM-CO_2-P" consists of following steps:

(a) grinding the "CHEM-CO_2"into a fine powder;

(b) mixing the powder of step (a) above with an aqueous dispersion or aqueous solution of a suitable inorganic or organic binding material;

(c) partially drying the powder-binder mix to yield a plastic-like material of desired consistency;

(d) forming the plastic-like mix of powder-binder into mechanically strong shaped articles "CHEM-CO_2-P" either by compression molding in a pelleting press or by extrusion molding with a suitable extruder; and

(e) totally drying the pellets or extrudates at a temperature of about 80° C to about 150° C in air atmosphere or at ambient temperature for a prolonged time.

11. A process as claimed in claim 1 and 10 wherein said binding material is selected from the group consisting of inorganic binders such as bentonite clay, attapulgite clay, kaolin clay, sepiolite clay, silica sol and combinations thereof, or from the group consisting of thermoplastic organic polymers such as polyvinyl alcohol, polypropylene, polyethylene and combinations thereof, or from the group consisting of gellable organic binders such as methylcellulose, ethylcelluose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxybutylcellulose, carboxymethylcellulose, and mixtures thereof, the most preferred binders being clay materials used alone or in combination with an organic binder selected from materials specified above as a co-binder.

12. A process as claimed in claim 1,10, and 11 wherein said binding material is used in the amount ranging from 5 to 30% based on the weight of CHEM-CO_2.

13. A process as claimed in claim 1 wherein CHEM-CO_2 obtained in the capturing reaction is $CaCO_3$ or an admixture of $CaCO_3$, $Ca(OH)_2$ and CaO, the composition of admixture being dependent on the temperature at which capturing process is carried out.

14. A process as claimed in claim 1,10,11 and 13 wherein the CHEM-CO_2 (e.g. $CaCO_3$) is transformed into shaped articles (CHEM-CO_2-P) by using bentonite clay as binding material and by compression molding in a pellet press.

15. A process as claimed in claim 1, 10, 11 and 13 wherein CHEM-CO_2 (e.g. $CaCO_3$) is transformed into shaped articles (CHEM-CO_2-P) by using polyvinyl alcohol as binding material and by compression molding in a pellet press.

16. A process as claimed in claim 1,10, 11, 12 and 14 wherein said bentonite clay binder is used in the amount of 20%, based on the weight of $CaCO_3$.

17. A process as claimed in Claim 1, 10, 11,12 and 15 wherein said polyvinyl alcohol binder is used in the amount of 5%, based on the weight of $CaCO_3$.

18. A process as claimed in claim 1 and 14 wherein the shaped articles (CHEM-CO_2-P) possess mechanical strength of at least 7 kg/cm^2.

19. A process as claimed in 1 and 15 wherein the shaped articles (CHEM-CO_2-P) possess mechanical strength of at least 10 kg/cm^2.

20. A process as claimed in claim 1 and 14 wherein the shaped articles (CHEM-CO_2-P) so prepared are thermal stable (no re-release of CO_2, and maintaining the physical integrity) upto a temperature of at least 500° C.

21. A process as claimed in claim 1, 14 and 15 wherein CHEM-CO_2 (e.g. $CaCO_3$) can be transformed into different coloured articles of CHEM-CO_2-P by adding a variety of colouring additives in small quantities during the processing, said colouring agents being added to boost marketability of CHEM-CO_2-P.

22. A process as claimed in 1 wherein said capturing step can be carried out in a batch, static or flow reactor system.

23. A process as claimed in claim 1 wherein said capturing step can be carried out by placing the capturing agent of this invention in the path of emission stream directly or after a conventional separation-recovery unit.

24. A process as claimed in claim 1 wherein the sources from which CO_2 can be mitigated and utilized is not limited to only those major kinds specified in claim 9 but may include relatively less CO_2 producing sources such as mining, metallurgical, fertilizer and cement manufacturing processes.

25. A process as claimed in claim 1 wherein value added products (CHEM-P-CO_2) obtained by the transformation of chemically captured CO_2 (CHEM-P) using binding agents of this invention as specified in claim 11 can be suitably modified by admixing with

thermoplastic or thermosetting materials in the extrusion process for specific applications.

26. A process as claimed in claim 1, 10, 11, 16 and 17 wherein said binders or their combination used may vary according to the weight of CHEM-CO_2.

27. A process as claimed in claim 1 which can also be applied to treating sources where a mixture of CO and CO_2 are produced in the combustion process via placing a regenerable oxidant catalyst such as CuO ahead of capturing agent which would convert CO to CO_2 and affect the capture.

28. A process as claimed in claims 1, 10, 11 and 13 which is environmentally friendly as the capturing agents such as $Ca(OH)_2$ and binding agents such as clays do not harm the environment, and as the articles made during CO_2 fixation process, after many years of usage, if desired, can be easily disposed as natural occurring substances without loss of CO_2.

29. A process as claimed in claim 1 wherein CO_2 is first recovered from the flue gas in a membrane separator in which membrane elements are arranged according to a preferred plate-and-frame configuration and then separated CO_2 is captured using the capturing agents of this invention and finally utilized by transforming chemically captured CO_2 (CHEM-CO_2) into value added commodites (CHEM-CO_2-P) in accordance with this invention.

30. A process as claimed in claim 1, 10 and 29 wherein said value added articles or commodities (CHEM-CO_2-P) is not limited to applications in household decorating, business and office machines, scientific and electronic equipments, reinforced plastics and engineering fields only.

31. A process as claimed in claim 1 and 9 which is also applicable to capturing and removal of SO_2 from flue gas streams present therein as a contaminant and then processed along with CHEM-CO_2 to value added articles (CHEM-CO_2-P).

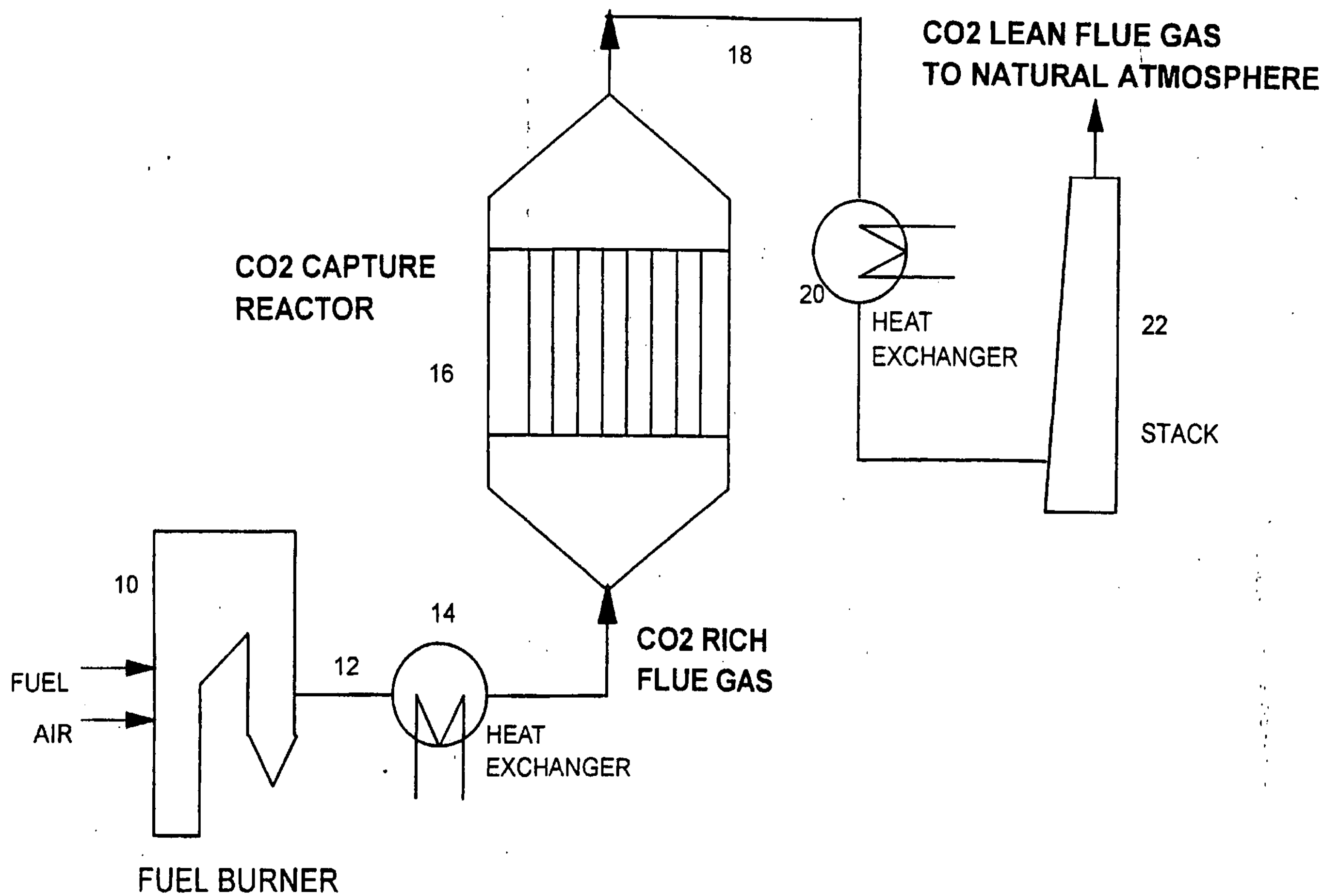
CO2 LEAN FLUE GAS
TO NATURAL ATMOSPHERE
18
CO2 CAPTURE
REACTOR
16
20
HEAT
EXCHANGER
22
STACK
10
14
12
FUEL
AIR
CO2 RICH
FLUE GAS
HEAT
EXCHANGER
FUEL BURNER

FIG.1

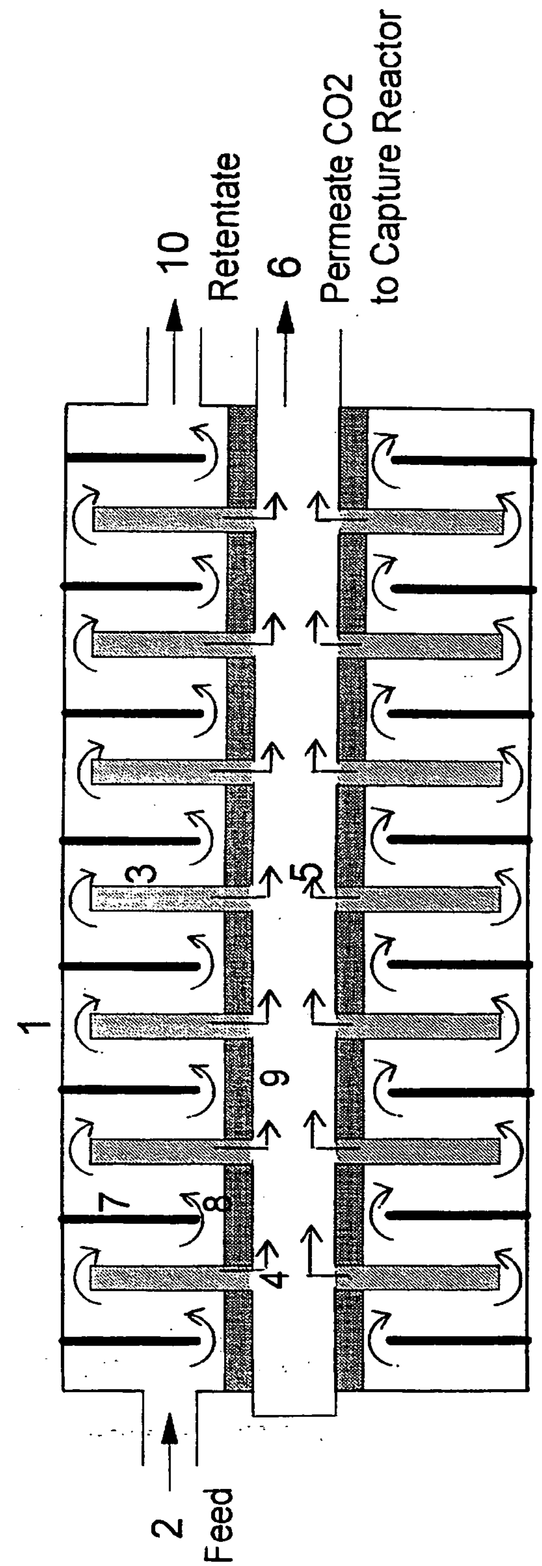
10
Retentate
6
Permeate CO2
to Capture Reactor
1
3
5
9
7
8
4
2
Feed

FIG. 2

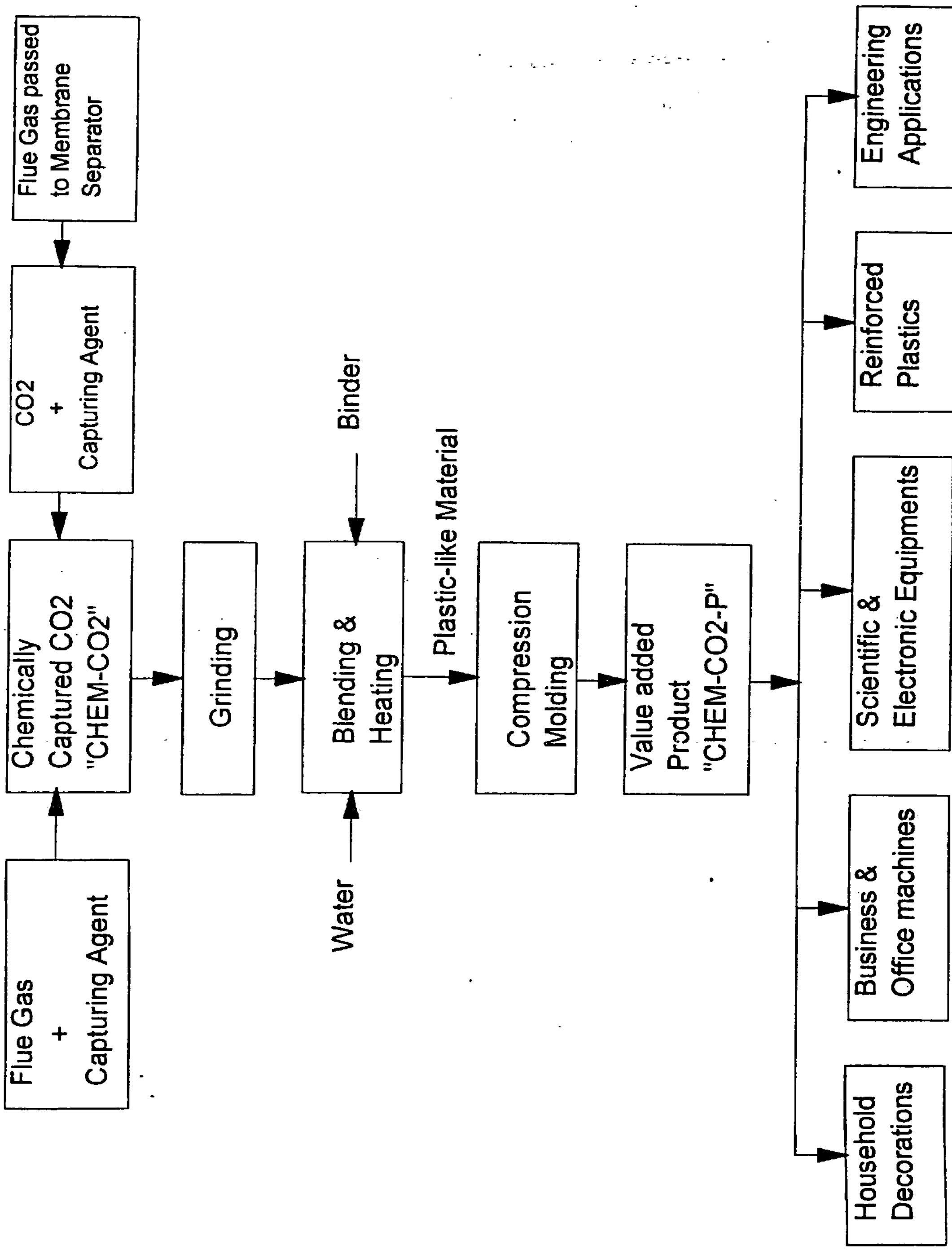
Flue Gas passed to Membrane Separator
CO2 + Capturing Agent
Flue Gas + Capturing Agent
Chemically Captured CO2 "CHEM-CO2"
Grinding
Binder
Water
Blending & Heating
Plastic-like Material
Compression Molding
Value added Product "CHEM-CO2-P"
Household Decorations
Business & Office machines
Scientific & Electronic Equipments
Reinforced Plastics
Engineering Applications

FIG. 3